

Importance of relativistic effects in electronic structure and thermopower calculations for Mg_2Si , Mg_2Ge , and Mg_2Sn

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We present a theoretical study of the influence of relativistic effects on the electronic band structure and thermopower of Mg_2X ($X = \text{Si}, \text{Ge}, \text{Sn}$) semiconductors. The full potential Korringa-Kohn-Rostoker (KKR) method is used, and a detailed comparison between the fully relativistic and semirelativistic electronic structure features is done. We show that the spin-orbit (S-O) interaction splits the valence band at Γ point in good agreement with the experimental data, and this effect strongly depends on X atom. The S-O modifications of the topology of the Γ -centered holelike Fermi surface pockets lead to a change in electron transport properties, which are investigated using the Boltzmann approach. In addition, a simple and efficient method is presented for the calculation of density of states effective mass m^* , and then used to examine the impact of relativistic effects on m^* . It is found that the S-O coupling of the valence bands reduces the effective mass and therefore significantly lowers the thermopower, primarily in Mg_2Sn , but also in Mg_2Ge . A detrimental influence of the S-O interaction on the thermoelectric performance of p -type Mg_2X is analyzed as a function of temperature (10–900 K) and carrier concentration (10^{18} – 10^{22} cm^{-3}). Interestingly, similar calculations in n -type Mg_2X , show a negligible effect of the S-O interaction on the lowest conduction bands and, consequently, also on the Seebeck coefficient.

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I. INTRODUCTION

The well-known Mg_2X ($X = \text{Si}, \text{Ge}, \text{Sn}$) thermoelectric compounds [1,2] and their alloys [3–5] have attracted renewed attention [6,7] as they are composed of abundant, low-cost (except germanium), and relatively nontoxic elements. These compounds exhibit a large Seebeck coefficient (S), quite high electrical conductivity (σ), and low thermal conductivity (κ), yielding high efficiency of thermoelectric (TE) conversion, which is commonly captured in the dimensionless figure of merit $zT = \frac{\sigma S^2}{\kappa} T$ (T is the absolute temperature). The fact that some of these materials have $zT > 1$ in the midtemperature range (400–800 K) and the lowest density among all efficient thermoelectrics [8], may prove to be decisive for ground transportation and space applications of these materials [9].

In particular, n -type $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$ solid solutions have been found to be the most favorable in terms of TE energy conversion as they have the lowest thermal conductivity due to the maximum mass difference between its components and quite large effective mass of carriers [6]. It was reported that more complex quaternary solid solutions $\text{Mg}_2\text{Si}_{1-x-y}\text{Sn}_x\text{Ge}_y$ exhibited even better TE performance upon n -type doping ($zT \sim 1.4$) [10]. Conversely, p -type Mg_2Si -based materials show markedly poorer TE performance ($zT < 0.4$) and there are only few impurities (Ga[11] or Ag[7,12]) that allow to turn these systems to the holelike electrical conductivity and positive thermopower.

In order to elucidate the unusual electron transport properties of $\text{Mg}_2(\text{Si-Ge-Sn})$ thermoelectrics, *ab initio* electronic structure calculations have been recently reported [13–16]. They mostly focused on the so-called convergence of two conduction bands [13,16,17], which appeared near X point in the Brillouin zone of $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$ for $x \sim 0.7$. Indeed, this

electronic structure feature, expected to be responsible for the overall enhancement of TE properties of these compounds, was supported by computations of relevant transport coefficients within the Boltzmann transport theory [14,16], but neglecting relativistic effects. We will show that the S-O interaction is crucial to reliably interpret especially p -type materials. Other theoretical works attempted to search for efficient n and p dopants to allow tuning and optimizing TE properties of these materials [9,18].

This work presents results of first-principles calculations performed by fully relativistic and semirelativistic Korringa-Kohn-Rostoker (KKR) methods combined with the Boltzmann transport approach to calculate thermopower as a function of temperature and carrier concentration. We show that the S-O interaction strongly affects the top valence bands near Γ point (best seen in Mg_2Sn) and the calculated values of the S-O splitting remain in good agreement with available experimental data. On the whole, the S-O coupling has a detrimental effect on p -type thermopower even at elevated temperature (300–400 K) and near optimal carrier concentration ($\sim 10^{20}$ cm^{-3}). On the other hand, the influence of the S-O coupling on conduction bands in n -type Mg_2X is negligible whatever temperature and carrier concentration.

The paper is organized as follows. Key formulas connecting the electronic band structure obtained from Korringa-Kohn-Rostoker (KKR) method and the electron transport coefficients studied within the Boltzmann approach, as well as computational details, are given in Sec. II. Section III presents our results containing mainly (i) an analysis of the holelike and electronlike Fermi surface shapes, (ii) a determination of effective mass of carriers using a simple and efficient procedure, and (iii) a discussion of Seebeck coefficient versus temperature and concentration. All results derived from semirelativistic and fully relativistic KKR calculations are compared in a systematic way. The paper is concluded in Sec. IV.

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TABLE I. The energy band gap in Mg_2X compounds calculated within LDA (E_g^{LDA}) from fully relativistic (FR) or semirelativistic (SR) KKR methods and compared to experimental values (E_g^{exp}) [29]. Experimental lattice constants [6] (a) are also given.

| | a (Å) | E_g^{LDA} (eV) | | E_g^{exp} (eV) |
|------------------------|---------|-------------------------|-------|-------------------------|
| | | SR | FR | |
| Mg_2Si | 6.336 | 0.32 | 0.33 | 0.78 |
| Mg_2Ge | 6.385 | 0.21 | 0.23 | 0.72 |
| Mg_2Sn | 6.765 | -0.17 | -0.25 | 0.35 |

II. THEORETICAL DETAILS

A. KKR band structure

The full potential KKR [19–24] method based on the Green's function multiple scattering theory was implemented to calculate the electronic band structure. The reduction of the Dirac equation to the so-called semirelativistic (SR) version was done by adopting the technique developed by Koelling and Harmon [25] and extended by Ebert [26]. With this procedure the resulting set of coupled radial equations after dropping the spin-orbit interaction is similar to the nonrelativistic one but retains all other kinematic effects such as mass-velocity, the Darwin contribution, and higher-order terms. The fully relativistic (FR) method was done by directly solving the four-component Dirac equation without any simplification. This allows to calculate the band structure with or without S-O interaction, showing its influence directly. The details of the electronic structure calculations were previously presented [23,27].

As already discussed in literature [14,31], LDA (and GGA as well) tends to underestimate band gaps also in Mg_2X compounds. In recent works [9,14], it was shown that the application of the modified Becke-Johnson semilocal exchange potential of Tran and Blaha [31] yielded gap values close to the experimental ones but without important changes in the shape of bands. Thus, in this work, the standard LDA (with the Perdew and Wang [28] formula for exchange-correlation potential) is employed in KKR calculations and the energy gaps are expanded to the experimental values [29] (see Table I) to allow for a reasonable discussion of transport properties as a function of temperature.

B. Electron transport

The Boltzmann transport theory, which can successfully connect atomic level properties of materials with the macroscopic transport coefficients [16,33–35] is used for the calculation of thermopower. Within this approach [32], the Seebeck coefficient can be expressed as

$$S = -\frac{1}{eT} \frac{\mathcal{L}^{(1)}}{\mathcal{L}^{(0)}}, \quad (1)$$

where

$$\mathcal{L}^{(\alpha)} = \int d\mathcal{E} \left(-\frac{\partial f}{\partial \mathcal{E}} \right) (\mathcal{E} - \mu_c)^\alpha \sigma(\mathcal{E}). \quad (2)$$

$\sigma(\mathcal{E})$ is an energy-dependent conductivity, commonly called the transport function (TF). The chemical potential $\mu_c = \mu_c(T, n_d)$ depends on temperature (T) and doping (n_d), where

an extra carrier concentration n_d can be positive (n -type doping, e.g., Sb or Bi in Mg_2X) or negative (p -type doping, e.g., Ga in some $\text{Mg}_2(\text{Si-Ge})$ alloys [11]). In the present work, the rigid band model [36] is used to mimic n -type and p -type behaviors, which allows to focus on the S-O effect on the charge carrier transport in case of electronlike and holelike doping, respectively.

The transport function, within the relaxation time approximation, has the form of a \mathbf{k} -space integral over n electronic bands [32]:

$$\sigma(\mathcal{E}) = e^2 \frac{1}{3} \sum_n \int \frac{d\mathbf{k}}{4\pi^3} \tau_n(\mathbf{k}) \mathbf{v}_n(\mathbf{k})^2 \delta[\mathcal{E} - \mathcal{E}_n(\mathbf{k})], \quad (3)$$

where τ is the electron relaxation time and $\mathbf{v}_n(\mathbf{k}) = \hbar^{-1} \nabla_{\mathbf{k}} \mathcal{E}_n(\mathbf{k})$ denotes the electron velocity. Representing the band structure as isoenergetic surfaces [37] [$\mathcal{E}_n(\mathbf{k}) \rightarrow S_n(\mathcal{E})$] and employing the commonly used constant relaxation time approximation [$\tau_n(\mathbf{k}) = \tau_0$] allows to convert TF into a form more convenient for numerical computation:

$$\sigma_\tau(\mathcal{E}) = \tau_0 \frac{e^2}{\hbar} \frac{1}{3} \sum_n \int_{S_n(\mathcal{E})} \frac{dS}{4\pi^3} |\mathbf{v}[S_n(\mathcal{E})]|. \quad (4)$$

It is worth mentioning that upon substituting Eq. (4) into Eqs. (3) and (2), τ_0 cancels out so that thermopower is independent of τ_0 in the constant relaxation time approximation.

In a similar way, the density of states (DOS) function can be calculated,

$$g(\mathcal{E}) = \sum_n \int_{S_n(\mathcal{E})} \frac{dS}{4\pi^3} \frac{1}{|\nabla_{\mathbf{k}} \mathcal{E}_n(\mathbf{k})|}, \quad (5)$$

and such representation enables to decompose the DOS (and also TF) into contributions from each n th band.

To facilitate the discussion of the Seebeck coefficient, the effect of the S-O interaction on the effective mass is investigated. Accordingly, we propose a simple and efficient way of calculating the energy dependent effective mass. DOS effective mass is defined for the parabolic band $\mathcal{E}(\mathbf{k}) = \hbar^2 \mathbf{k}^2 / 2m$ through the formula:

$$g(\mathcal{E}) = \frac{m}{\hbar^2 \pi^2} \sqrt{\frac{2m\mathcal{E}}{\hbar^2}}. \quad (6)$$

To generalize this concept to any other, nonparabolic case, the effective mass becomes energy (or carrier concentration) dependent $m = m(\mathcal{E})$. The effective mass can be extracted from the DOS formula and combined with its energy derivative

$$m(\mathcal{E}) = m_e m^*(\mathcal{E}) = \hbar^2 \sqrt[3]{\pi^4 g(\mathcal{E}) g'(\mathcal{E})}, \quad (7)$$

where m_e denotes free electron mass.

In this way, the dimensionless DOS effective mass (m^*) can be found at every energy point, at which DOS was calculated. This approach can also be seen as fitting the effective mass with the parabolic band at \mathcal{E} and \mathbf{k} points separately and then averaging over the isoenergy surface $S_n(\mathcal{E})$. Practically, the computation of m^* using this scheme requires a highly accurate DOS function to avoid problems with numerical noise appearing when differentiating. Here, DOS is calculated with $\Delta\mathcal{E} \sim 9$ meV energy resolution, and the $m^*(\mathcal{E})$ resulting from Eq. (7) in the final step is smoothed by convolution

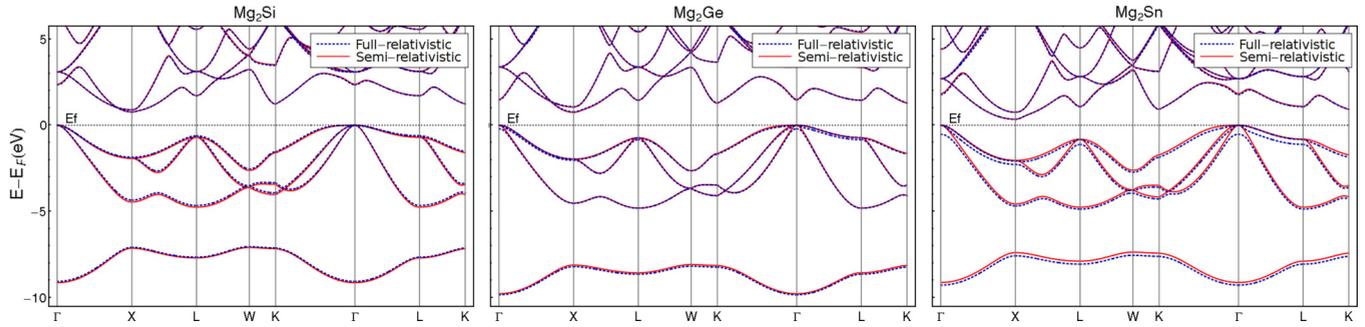


FIG. 1. (Color online) Electron dispersion curves for Mg_2Si (left), Mg_2Ge (middle), and Mg_2Sn (right) as resulted from semirelativistic and fully relativistic KKR calculations. In each figure, the Fermi level E_F was shifted to the top of the valence bands (Γ point) and the energy gaps were expanded to the experimental values (see text and Table I).

with a Gauss function with standard deviation $3 \times \Delta\mathcal{E}$. A comparison of the raw and smoothed results is done in Fig. 4.

III. RESULTS

A. Band structure

Electronic band structures of Mg_2X as calculated from the fully relativistic (FR) and semirelativistic (SR) KKR methods, are shown in Fig. 1. Generally, the electronic structure below the energy gap consists of four occupied bands. The lowest lying and separate band, essentially of s symmetry, is located well below the Fermi energy and the other three bands are forming the main block of valence states (strongly hybridized s -Mg and p -X states), with the bands maxima at the Γ point in the Brillouin zone (BZ). These three bands are labeled as heavy-hole (HH), light-hole (LH), and split-off (SO) bands, respectively.

The spin-orbit coupling removes the band degeneracy at Γ point, pushing the SO band down in energy in different way in Mg_2X compounds. The conduction bands have the lowest energy value at the X point in BZ, yielding an indirect band gap in all Mg_2X compounds. It was shown [6,16] that the relative

position of the two lowest conduction bands mutually change with X atom in Mg_2X , which is clearly seen in the Fig. 1.

As expected, the importance of relativistic effects gradually increases with increasing atomic number of the X element. In Fig. 1, the difference between SR and FR, as induced by the S-O coupling, can be easily detected for Mg_2Sn and also Mg_2Ge , while it is hardly visible in this energy range for Mg_2Si . The S-O interaction manifests most strongly for the valence bands around the Γ point. It is best seen in Fig. 2 where tentatively three relativistic effects can be observed.

The first effect (as above-mentioned) is removing the degeneracy of electronic states at Γ point by the S-O splitting, Δ_{S-O} , of the $p^{3/2}$ and $p^{1/2}$ orbitals. As a result, the SO band is moved towards a lower energy with the Δ_{S-O} values (see Table II) strongly increasing with the atomic number of X atom. Starting from $\Delta_{S-O} = 36$ meV in Mg_2Si , through $\Delta_{S-O} \simeq 208$ meV in Mg_2Ge , the largest $\Delta_{S-O} \simeq 525$ meV is reached in the heaviest Mg_2Sn compound. Overall, a good agreement between the KKR results and the experimental data derived from infrared spectroscopy measurements is found.

The second modification of the band structure of Mg_2X induced by the S-O interaction, is removing of HH and LH band degeneracy, which appears in some BZ parts (e.g., along

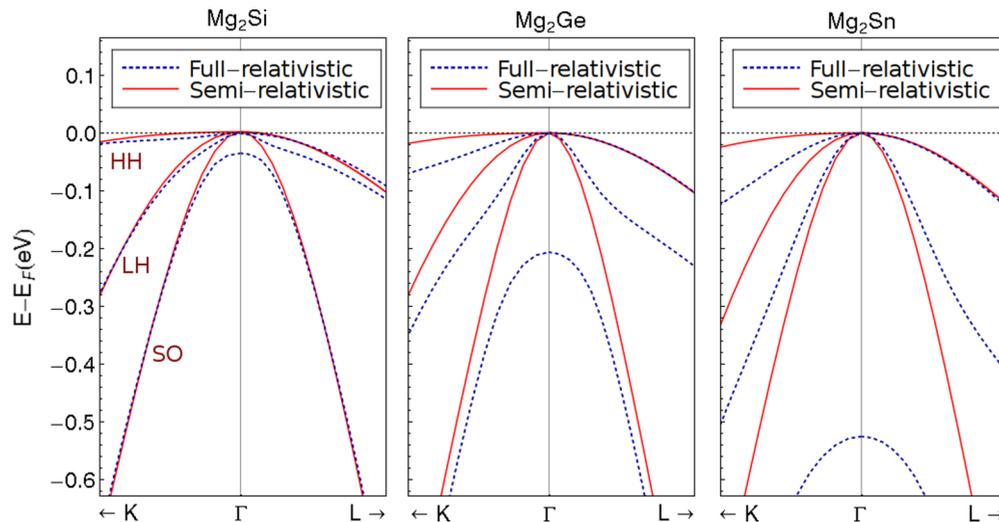


FIG. 2. (Color online) Zoom of the three valence bands of Mg_2X along the K - Γ - L direction as computed from SR and FR calculations. The spin-orbit interaction removes the degeneracy of bands at Γ , and the largest splitting is observed for the Sn case. Subtle topological effects are evidently detected for the LH band (see text).

TABLE II. The values of spin-orbit splitting at Γ point in Mg_2X compounds.

| | Mg_2Si | Mg_2Ge | Mg_2Sn |
|------------------|------------------------|------------------------|-------------------------------------|
| Calculated (meV) | 36 | 208 | 525 |
| Measured (meV) | 30 ^a | 200 ^a | 480 ^a , 600 ^b |

^aReference [38].

^bReference [39].

Γ - L - X directions) from the semirelativistic KKR calculations. This splitting is smaller, comparing to the splitting of $p^{3/2}$ and $p^{1/2}$ orbitals at Γ , however, at the L point it can also reach considerable values, i.e., 287 meV ($X = \text{Sn}$), 118 meV ($X = \text{Ge}$), and 23 meV ($X = \text{Si}$).

The third and also the most subtle effect, visible actually on an enlarged scale only (Fig. 2), is related to the modification of the bands shapes, which at a first glance suggests a decrease of m^* (as discussed below). On the whole, the three aforementioned effects are expected to markedly influence thermopower behaviors in Mg_2X compounds (see Sec. III B).

The magnitude of overall relativistic effects as well as the S-O splitting of the band structure near the Γ point is well illustrated in Fig. 3, where Fermi surfaces (FS) for Mg_2Sn at a hole concentration $p = 10^{21} \text{ cm}^{-3}$ are plotted. A similar comparison of FR and SR results for p -type Mg_2Si and also Mg_2Ge shows less pronounced details on the corresponding FS and is not presented. We see that the high velocity (red color in the Fig. 3) hole pocket centered at Γ becomes the SO band pocket and is shifted out of the Fermi surface at the hole concentration $p = 10^{21} \text{ cm}^{-3}$. Also, the change in the FS curvature can be easily noticed.

The S-O interaction effects, as described above, first of all, lower the DOS near the valence band edge. This is accompanied by a decrease of the DOS effective mass, which likely reduces the thermopower. The effective mass calculated with the use of Eq. (7) is shown in Fig. 4. The reduction of m^* by the S-O interaction is clearly seen for the Mg_2Ge and Mg_2Sn compounds, where it reaches around 50% (dropping from ~ 1.1 to $\sim 0.5 m_e$ in the latter). Such an important reduction can not be explained by the shift of the high velocity SO band, and the change of mass is mainly attributed to

modification of the $\mathcal{E}(\mathbf{k})$ slope of the HH and LH bands (see Fig. 2). The bottom-right panel in Fig. 4 shows the effective mass of p -type Mg_2Sn as resulted from the FR and SR calculations, decomposed into all three band contributions. This clearly evidences, that actually the whole contribution to the effective mass comes from the HH band. Bearing in mind that effective mass is an additive quantity due to formula $m_{\text{all}}^* = (\sum_i m_i^{*3/2})^{2/3}$, the modification of the band curvature by the S-O interaction is the most important effect for the decrease of m^* , more significant than the splitting of bands near Γ . The same can be concluded from Fig. 5, where the reduction of total DOS (g) is much larger than the SO band contribution, which is very low due to high velocity ($g \sim 1/v$).

We can also notice an interesting topological feature of the dispersion relations in the FR case: the LH band is convex along the Γ - L direction, close to the valence band edge. In the SR case, the flexion point, at which the $\mathcal{E}(\mathbf{k})$ function changes from convex to concave, lies at much deeper energy. The S-O interaction moves this flexion point in the energy (and carrier concentration) range important for the TE properties. This convex $\mathcal{E}(\mathbf{k})$ function locally leads to a positive effective mass, i.e., there is an electronlike, compensating contribution to the overall holelike electronic properties. This FS feature reduces the LH band effective mass, being another source of lowering of m^* . This behavior resembles the case of PbTe-PbS alloy [30], where a similar topological effect of the local convex shape of the valence band leads to a negative Seebeck coefficient at low temperatures.

In Mg_2Ge compound, the HH band modifications as well as energy splitting of the bands are smaller than in Mg_2Sn , and, as a consequence, the effective mass reduction is limited to the narrow energy range near the valence band edge.

In Mg_2Si , the effect is opposite to the previously discussed cases. A fully relativistic treatment yields about a 10% rise of the value of the effective mass due to the $\mathcal{E}(\mathbf{k})$ slope change, except for the range just below the valence-band edge, where the SO band moves out and a local convex $\mathcal{E}(\mathbf{k})$ function shows up.

The analysis of the effective mass suggests how the spin-orbit interaction will modify the thermopower of the system, since $S \propto m^*$. For the Mg_2Sn , we may expect a strong reduction of the p -type thermopower, for the Mg_2Ge , the reduction of thermopower is expected only at low concentration in p -type

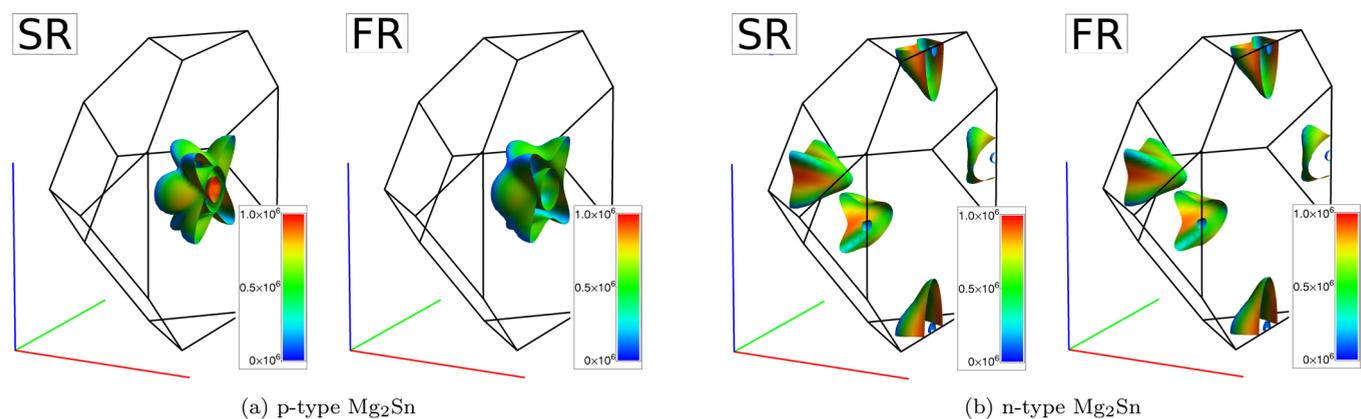


FIG. 3. (Color online) Fermi surfaces of p -type (a) and n -type (b) Mg_2Sn plotted for carrier concentration 10^{21} cm^{-3} . In both cases, semirelativistic (SR) and fully relativistic (FR) results are compared. Electron velocities (in m/s) are represented by colors.

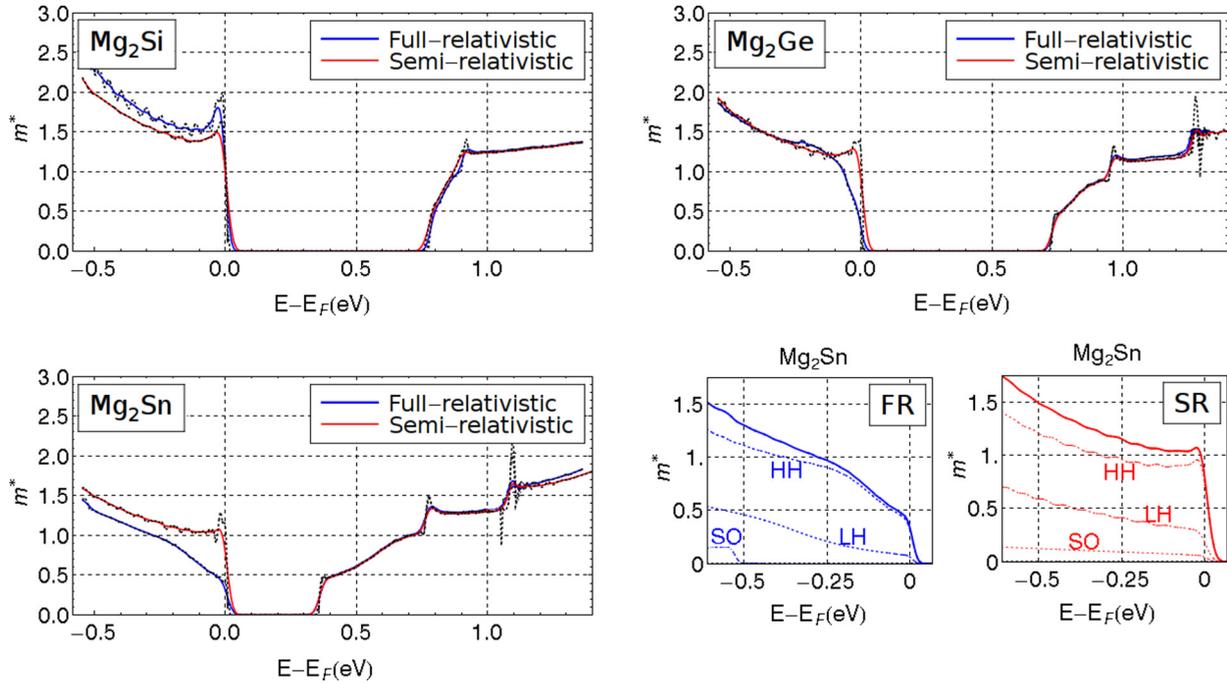


FIG. 4. (Color online) DOS effective mass of carriers near the band gap in Mg_2X compounds. Bottom-right panel shows the effective hole mass corresponding to the heavy-hole (HH), light-hole (LH), and split-off (SO) bands for fully relativistic (FR) and semirelativistic (SR) results. The spin-orbit interactions mostly affect the mass of heavy holes.

materials, and an increase of the Seebeck coefficient for Mg_2Si can be predicted. The decrease of thermopower in Mg_2Sn system can also be deduced from the transport function in Fig. 5, where its strong decrease in p -type doping

is seen in the FR calculation. It is also worth noting that the SO band has negligible influence on the total TF (and therefore thermopower), which is not so evident accounting for the fact that TF is a function sensitive to electron's velocity ($\sigma \sim v^2$) and the SO band has the highest value of v up to $1.0 \times 10^6 \text{ ms}^{-1}$ (see next paragraph for detailed calculation of thermopower).

As far as the conduction bands are concerned, no significant difference between FR and SR calculations are observed, even in the case of Mg_2Sn . The Fermi surfaces and also the effective masses do not show any difference for n -type doping as large as $n = 10^{21} \text{ cm}^{-3}$ [see Figs. 3(b) and 4].

B. Thermopower

The thermopower of Mg_2X compounds, calculated in the constant relaxation time approximation and using Eqs. (1)–(4), is shown in a wide range of carrier concentration for both n and p types in Fig. 6. In addition, for the carrier concentrations $n = p = 10^{20} \text{ cm}^{-3}$ and at three selected temperatures (70, 300, and 900 K), the Seebeck coefficient values are gathered in Table III. The results of the Boltzmann transport and KKR calculations are consistent with intuitive predictions based on the aforementioned analysis of the band splitting and effective mass changes. First of all, for the three Mg_2X compounds, there is no significant difference between thermopower from FR and SR calculations in the n -type materials for high concentration and low temperature. The reason is simply the negligible differences between conduction bands induced by the S-O interaction. On the other hand, the difference between FR and SR appearing for lower carrier concentration and higher temperature comes from the bipolar

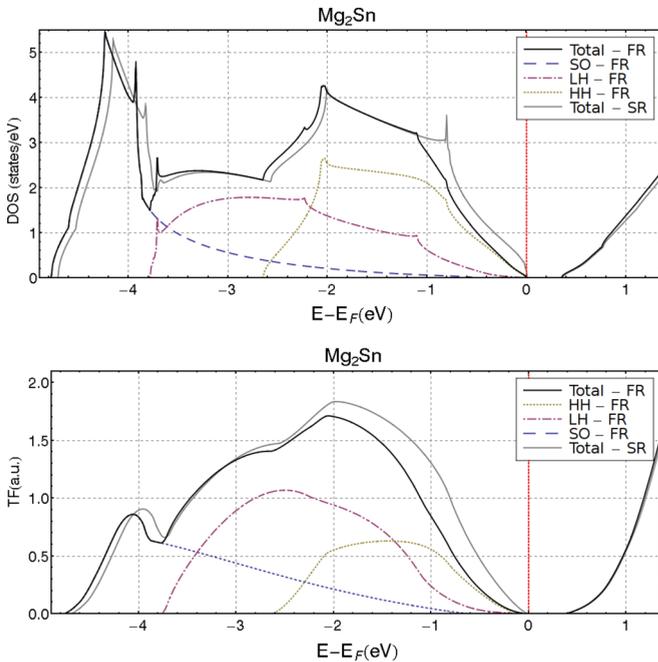


FIG. 5. (Color online) Density of states (DOS) and transport function (TF) of Mg_2Sn with a decomposition on bands calculated with the fully relativistic (FR) method. For comparison, DOS and TF are also shown for the semirelativistic (SR) case.

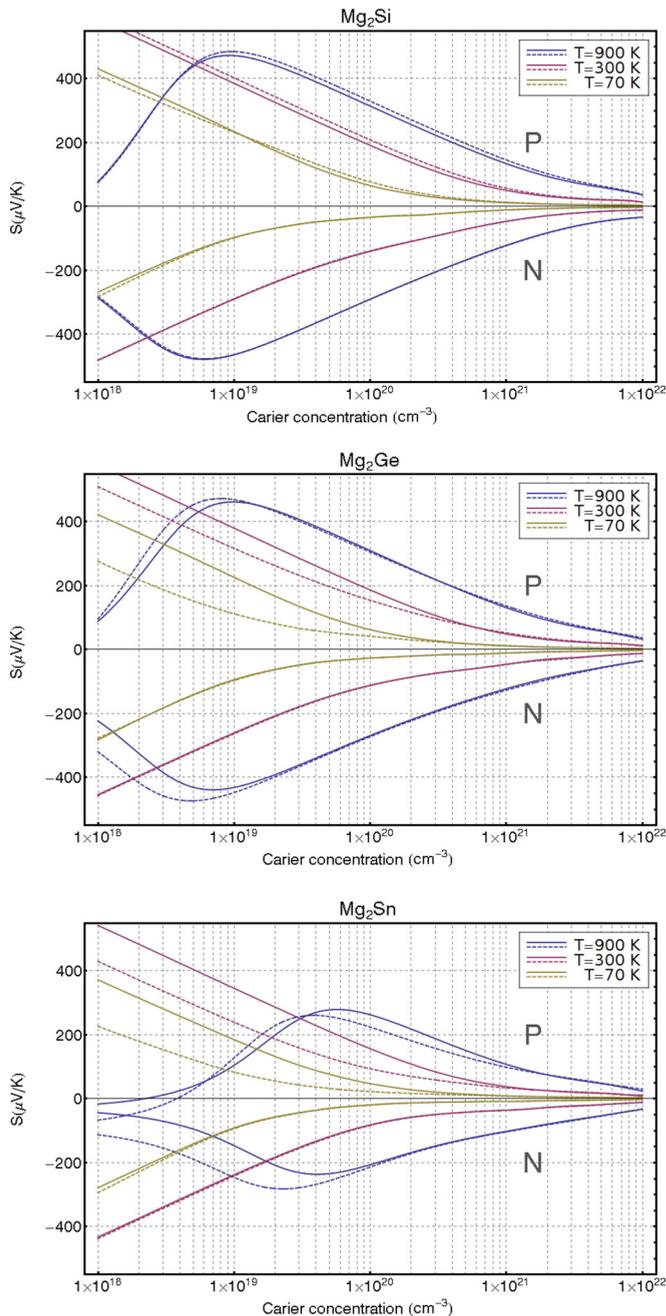


FIG. 6. (Color online) Thermopower of Mg_2Si (top), Mg_2Ge (middle), and Mg_2Sn (bottom) as a function of carrier concentration for selected temperatures. Solid lines show semirelativistic and dashed line fully relativistic results, respectively.

effect, which accounts for contribution from valence bands, which are apparently different from the FR and SR results. The bipolar reduction of the absolute value of n type S is highest for Mg_2Sn , where the band gap is the smallest. In the fully relativistic KKR calculations, the Seebeck coefficient is less reduced because of the lower effective mass of holes.

For holelike thermopower, the splitting of the bands accompanied by the reduction of the effective mass significantly decreases the Seebeck coefficient in Mg_2Ge and Mg_2Sn for

$p < 10^{21} \text{ cm}^{-3}$ in the low and midtemperature range (see also Table III). For Mg_2Sn , the S-O effect can lower the thermopower even twice, showing that it is crucial for the discussion of the TE properties of p -type Mg_2X systems. At high temperature, due to the temperature blurring of DOS (convoluted with Fermi-Dirac function), the main contribution to thermopower comes from the lower-lying parts of dispersion curves, where the computed band curvatures from FR and SR approaches are similar. Also, at high temperature, the importance of the SO band splitting diminishes, which effectively lowers the difference between SR and FR computations. A similar trend is apparently observed when the carrier concentration increases and the Fermi level moves deeper into the valence bands and almost no difference between SR and FR results is observed for $p > 10^{21} \text{ cm}^{-3}$.

Interestingly, FR KKR calculations show that in p -type Mg_2Si , both m^* and S values are, in principle, higher than the values from the SR computations. The slightly reduced S is seen only in very low concentration and temperature, where the small area of FS near Γ point is taken into consideration in electron transport. In this case, i.e., $p < 1 \times 10^{19}$, the band curvature modification as well as the S-O splitting, seen in Fig. 2, leads to the decrease of m^* , and therefore to a small decrease of S (see Fig. 6 at $T = 70 \text{ K}$ and small hole concentration p). For $p > 1 \times 10^{19}$, these effects are no longer important. At higher temperature, the S-O splitting is too small and additionally smeared by temperature, i.e., $\Delta_{\text{S-O}} = 30 \text{ meV} = k_B T$ for $T \sim 350 \text{ K}$, which does not alter the results from the transport function integration [Eq. (1)].

IV. SUMMARY

The results of electronic band structure calculations with the use of a fully relativistic (FR) versus semirelativistic (SR) full potential KKR method for the Mg_2X ($X = \text{Si}, \text{Ge}$ and Sn) compounds were reported. It was found that the S-O interaction splits the valence band structure, with the S-O splitting at Γ point, namely 36, 208, and 525 meV, well corresponding to experimental data [38,39] of 30, 200, and 480 meV (or 600 meV) in Mg_2Si , Mg_2Ge , and Mg_2Sn , respectively. The S-O splitting itself, as well as the modification in the dispersion relation (even more important) of the top valence bands, i.e., heavy- and light-hole bands, significantly decreased the effective mass and the Seebeck coefficient. In Mg_2Ge and Mg_2Sn , the analysis of the energy dependent DOS effective mass shows that the S-O interaction lowers m^* of holes, and the effect is larger near the valence band edge and for the heaviest compound. In general, this leads to the reduction of the p -type thermopower, mostly at lower concentration and low or medium range of temperature. The thermopower decrease becomes more serious with increasing atomic number of X element, reaching the magnitude of 50% in Mg_2Sn . On the whole, our KKR calculations combined with the Boltzmann transport approach clearly show that the relativistic effects are detrimental for the thermoelectric performance in p -doped Mg_2Ge and Mg_2Sn . In Mg_2Si , the S-O interaction slightly increases the effective hole mass, except for the low carrier concentration range. This behavior leads to a small increase of thermopower (up to 10%) for $p > 10^{19} \text{ cm}^{-3}$.

TABLE III. Seebeck coefficient (FR and SR results) at $n = p = 10^{20} \text{ cm}^{-3}$ for different temperatures in Mg_2X compounds.

| | | Mg_2Si | | | Mg_2Ge | | | Mg_2Sn | | |
|----------|---|------------------------|-------|-------|------------------------|-------|-------|------------------------|-------|-------|
| | | 70 K | 300 K | 900 K | 70 K | 300 K | 900 K | 70 K | 300 K | 900 K |
| n type | S_{fullrel} ($\mu\text{V}/\text{K}$) | -33 | -139 | -291 | -27 | -113 | -273 | -20 | -84 | -214 |
| | S_{semirel} ($\mu\text{V}/\text{K}$) | -34 | -141 | -290 | -27 | -112 | -269 | -19 | -82 | -207 |
| | $S_{\text{FR}}/S_{\text{SR}}$ (-) | 98% | 99% | 100% | 100% | 101% | 101% | 103% | 102% | 104% |
| p type | S_{fullrel} ($\mu\text{V}/\text{K}$) | 77 | 208 | 329 | 41 | 154 | 305 | 22 | 94 | 224 |
| | S_{semirel} ($\mu\text{V}/\text{K}$) | 65 | 191 | 314 | 62 | 189 | 310 | 47 | 156 | 263 |
| | $S_{\text{FR}}/S_{\text{SR}}$ | 118% | 109% | 105% | 67% | 83% | 98% | 48% | 60% | 85% |

In turn, the S-O coupling effect on the conduction bands is negligible in all Mg_2X compounds. Surprisingly, the n -type thermopower at lower carrier concentrations benefits from the degradation of the p -type S due to the reduction of the bipolar effect, which is well seen in Mg_2Ge and Mg_2Sn compounds.

In summary, the fully relativistic KKR results revealed that the spin-orbit interaction is a significant factor decreasing the thermoelectric performance of p -type Mg_2X (especially Mg_2Sn). They also enlightened the reason why in $\text{Mg}_2(\text{Si-Ge-Sn})$ system the measured zT in p -doped samples was

much lower ($zT < 0.4$) [11] than the values gained in n -doped materials ($zT \sim 1.4$) [10,40].

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